

PROCESSES FOR THERMOCHEMICAL CONVERSION OF BIOMASS

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Abstract

An overview is given of traditional and new processes for thermochemical conversion of biomass, such as combustion, gasification, some versions of pyrolysis, and a series carried out in hot compressed water. The processes are all briefly described regarding the operating conditions, the possible feedstock materials and the desired products. Wherever appropriate, fundamental principles are addressed as well. The state of technology development varies a lot. While biomass combustion for combined heat and power is a mature technology, the hydrothermal processes are still being investigated in research laboratories to proof the principles. Gasification and pyrolysis processes are generally in a state of being demonstrated at a significant scale. While combustion, gasification and pyrolysis all need fairly dry feedstock materials, wet feedstock having moisture contents far over 50 wt.%, is often considered for conversion under hydrothermal conditions. Products, either being a gas, a liquid, or a carbonaceous solid always need further purification or upgrading before any end-use.

Keywords: biomass, thermochemical, hydrothermal, gasification, fast pyrolysis, torrefaction, supercritical, liquefaction, carbonization

Introduction

Fossil fuels like coal, crude oil and natural gas have been used for ages to provide the energy consumed by the world population. During the past decades, the awareness of risks and harmful consequences has increased, the main concerns being:

1. Emission of carbon dioxide, an important perpetrator of global warming
2. Depletion of the fossil fuel resources within a limited time period of 50 to 200 years
3. Dependency on fossil fuel supplying countries in politically unstable regions
4. Insecurity of supply by a lack of diversification in energy resources

A solution is offered by the use of renewable resources like wind, solar, hydro and biomass energy. Biomass is the name used for feedstock materials derived from trees and plants, including wood and residues from agriculture or plantations. Certain types of organic waste, from animals or from the food/feed industries are sometimes included in the definition.

The emission of carbon dioxide into the atmosphere is effectively avoided when biomass is used as a source of energy because the quantity of CO₂ released upon combustion of biomass products is the same as bound by the trees and plants during their growth. The biomass CO₂ cycle is relatively short and varies from 1 to 15 years. It is interesting to note that, by combining bioenergy production with CO₂ capture technologies, it is even possible to remove carbon dioxide from the atmosphere.

Thermochemical conversion of biomass is traditionally referring to processes in which the biomass is decomposed at high temperatures to produce char and vapors that can be:

completely burnt simultaneously to produce heat:	combustion	T > 800 °C
partially burnt to produce a combustible or synthesis gas:	gasification	T < 900 or T > 1250 °C
separated as bio-char and/or bio-oil (condensed vapors):	pyrolysis	T > 300 °C

Novel thermochemical processes recently under development include

biomass torrefaction to produce a more coal-like solid fuel	1 bar / 280 °C
production of biochar for soil improvement and carbon sequestration	1 bar / 400 to 700 °C
aqueous phase reforming of sugars, for hydrogen and alkanes/isoalkanes	50 bar / 250 °C
hydrothermal liquefaction to produce an oxygen poor bio-liquid	200 bar / 300 °C
gasification in supercritical water to produce pressurized synthesis gas	300 bar / 600 °C

Biomass combustion

Biomass consists of cellulose, hemi-cellulose, lignin, sugar, starch, lipids, fats, extractives and minerals. Before combustion, the edible parts are usually separated from the plant for food/feed or bio-fuels production. Depending on the type of biomass, the heat of combustion varies from 17 to 19MJ/kg on an ash-free dry basis. The combustion reaction for the main elements is represented by: $C_xH_yO_z + nO_2 \rightarrow x CO_2 + (y/2)H_2O$, with $n = x + (y/4) - (z/2)$ leaving carbon dioxide and water as the combustion products, next to released heat.

Plant nutrients, including elements like nitrogen, sulfur, phosphor, calcium, potassium, sodium and magnesium are causing the combustion process to be operated in a way avoiding any harmful consequences of ash melting (solids agglomeration leading to possible blocking of the furnace), and to include secondary equipment for the reduction of undesirable gaseous emissions.

Biomass combustion [1] is meant to produce heat for direct use, or for electricity production by steam raising and expansion over a turbine. Combustion is applied at all possible scales varying from small stoves for domestic cooking or heating, up to large scale power plants requiring an input of over a thousand tons of biomass per day. If electricity is demanded it is always desirable to sell the co-produced heat as well (CHP: combined heat and power) in order to achieve an acceptable efficiency level. Co-feeding or co-firing of biomass in coal based power stations is currently the most successful way of fossil fuel replacement by biomass in western countries. The total installed capacity in biomass power generation around the world is approaching 50,000 MW_e including also the combustion of biogas or landfill gas.

Biomass gasification

Gasification of biomass (CH_{1.4}O_{0.6}) is a thermochemical process including the degradation of its constituents to, ideally, the smallest possible molecules, CO and H₂. A pure mixture of carbon monoxide and hydrogen is suitable as feedstock for secondary catalytic synthesis of a variety of (oxygenated) hydrocarbons. It is therefore called synthesis gas, or briefly syngas. In many cases

however, the degradation is incomplete, causing the presence of CH_4 as well as of low (C_xH_y) and high (tars) molecular weight hydrocarbons in the gas. A raw product gas may also contain dust and gaseous derivatives of the biomass ash.

In case of direct gasification, part of the biomass is combusted by introducing air into the gasifier, thus providing the heat for maintaining the process. As a consequence, this product gas is diluted with a significant quantity (typically 50 volume percent) of nitrogen. A way to avoid this dilution is by indirect heating of the gasifier in a two-vessels reactor configuration, enabling the separation of combustion and gasification. The gasifier vessel is then blown exclusively by steam which can be separated afterwards from the produced gas by condensation. Air gasifiers and indirectly heated steam-blown gasifiers are operated at temperatures ranging from 750 to 850 °C which are below the ash melting temperatures. Ash is then collected as bottom ash or cyclone ash. As mentioned above, the indirectly heated steam-blown gasifier produces a gas that is free of nitrogen. Such a gasifier could, after a catalytic reforming step for the conversion of methane and tars, also deliver pure synthesis gas. However, in order to produce - in a single step - syngas that is free of nitrogen, methane and tars, high temperature gasification is required (> 1250 °C), while using oxygen or a mixture of oxygen and steam as the gasification agent. At such high temperatures ashes are melting and they are collected as slags in a quench bath.

Biomass gasification is a technology that has been developed and practiced over many decades, and for a wide variety of purposes. Handbooks [2] often refer to the utilization of small (on board) wood gasifiers for fuelling of vehicles during the second world war when petroleum fuels were not available. The type of gasifiers that are being used these days are fixed beds (downdraft and updraft), fluidized beds and circulating fluidized bed. While fluidized bed gasifiers can be used at a larger scale, the scale of application for fixed bed gasifiers is limited to approximately 1 MW thermal input. A special category of gasifiers is based on the entrained flow principle, where pulverized coal or heavy oil is blown into an empty space together with the gasification medium (oxygen or oxygen/steam). These entrained flow gasifiers are typically used in the oil refineries (hydrogen or syngas production) or for large scale power production (> 100 MW thermal input) by complex gas and steam turbines cycles. Wood derived fast pyrolysis oil has however been successfully gasified in entrained flow pilot gasifiers a number of times [3]. For solid biomass, a two stage system has been developed in the past years based on the high temperature gasification of biomass vapors and its char after a prior carbonization of the feedstock material in a first stage.

Regarding the issue of biomass based transportation fuels, there is indeed a distinct interest these days in developing biomass gasification for producing syngas of a quality sufficient for the production of methanol or higher alcohols, dimethylether, or Fischer Tropsch diesel. It includes multiple process steps starting with exhaustively cleaning of the raw biomass gas and followed by high temperature and high pressure catalytic conversions like reforming, water-gas shift and synthesis. To make this economical, large scale operation is likely required, which raises the question of cost-effective biomass collection.

Depending on the type of biomass feedstock that is gasified, and the type of gasifier itself, the raw product gas may contain contaminants either derived from impurities in the feedstock or generated in the process. The main ones are dust, tar, alkali's, chlorine, sulfur and nitrogen. Removal of these contaminants to a degree that depends on the application of the product gas is always required. Tar and particulates cannot be tolerated because they deposit on surfaces in heat exchangers and on prime mover components. Especially in syngas applications, where the gas is passed over catalysts that are sensitive to poisoning (e.g. by sulphur), exhaustive gas purification can add significantly to the complexity and costs of the gasification process. For further details on the cleaning of biomass derived gas, the reader is referred to a recent review by Woolcock and Brown [4].

After sufficient cleaning of the raw product gas, it can be used in more efficient prime movers for the conversion to electricity. Incomplete fuel oxidation and heat losses from the prime movers (mainly latent heat in exhaust gas) always cause a significant part of the oxidation reaction-enthalpy to be left in the combustion products. Indeed the electric efficiency of gas turbines and internal combustion engines is still limited to values below 45 %. The concept of combining a gas turbine with a steam turbine in an integrated combined cycle (IGCC: Integrated Gasification Combined Cycle) promises high electric efficiencies of more than 45 %, in cases where high-temperature gas turbines can be applied. Here, the heat contained in the gas turbine exhaust gas is used to generate steam for the steam turbine. Several coal based demonstration plant are in operation [5]; for biomass the demonstration is still in its infancy [6] . Oxygen blown entrained flow gasification at elevates pressures as used in coal IGCC plants, cannot be applied directly to biomass as a feedstock material. Moreover the presence of biomass specific minerals (alkali's) demands additional measures in the gas cleaning train.

Biomass pyrolysis

The word “pyrolysis” is used for the degradation of a substance upon exposure to high temperatures. Exclusion of air or oxygen is essential in case ignition and combustion of the primary products is considered undesirable. Fast pyrolysis and slow pyrolysis (including torrefaction) are thermochemical processes involving the conversion of biomass into predominantly a liquid or solid respectively.

Fast pyrolysis is generally employed to maximize the liquid bio-oil product yield, the benefit being that the bio-oil has a significant calorific value and the liquid may be handled with greater ease than conventional biomass. The bio-oil may be combusted directly or upgraded such that it may be used as a transportation fuel. The extraction of unique chemicals from the bio-oil is also a route for valorizing fast pyrolysis products.

In slow pyrolysis most of the volatiles are removed from the biomass to obtain charcoal, a smokeless fuel that is still used widely for cooking and heating purposes. Slow pyrolysis processes are tailored to maximize the yield of the solid product. Slow pyrolysis of wood at temperatures up to 450 °C is a process that charcoal makers have exploited for thousands of years. Charcoal has been used in industry as well, viz. in blast furnaces for making of iron. These days there is quite some interest in using slow pyrolysis char (biochar) for mixing into the soil. This is meant then to improve the soil structure and fertility and, at the same time, as method of carbon sequestration and storage. The promise of biochar as a valuable soil amendment for improving plant productivity and agriculture yields, coupled with the opportunity for inclusion into waste management and bio-energy schemes, have propelled the biochar idea into mainstream scientific discourse.

A very mild form of pyrolysis, carried out at temperatures around 300 °C, is called torrefaction. Here the pyrolysis is meant to just remove a small portion of the volatiles, viz. those derived from the degradation of the hemicellulose. The solids obtained differ from the original biomass in a number of ways, such as increased energy density, hydrophobicity, grindability and reduced biodegradability. These characteristics allow for improved handling, transport and utilization of the torrefied biomass within existing coal-based processes when compared to biomass.

Before the eighties of the last century, pyrolysis research was mostly dealing with the thermal decomposition of organic compounds, polymers, salts, etc. Besides, quite a number of papers can be found regarding coal pyrolysis (production of metallurgic coke), and some on the pyrolysis of oil shale. When searching the web of science for publications on “*biomass pyrolysis*” during the period 1955 to 1980, less than ten hits are obtained. Pyrolysis of cellulose, one of the main biomass constituents, was being investigated quite frequently, but just in relation to flame retardation purposes. Likewise some lignin pyrolysis studies from that period can be traced back, when wood chemistry scientists

were interested in the analysis of lignin vapors. When using the keywords “*biomass fast pyrolysis*”, just a single result is found for that period (abstract by J.P. Diebold, ACS Meeting, Aug. 1980), focused however on the production of olefins and other valuable hydrocarbons, rather than on condensable liquids. One may conclude that the science and development of biomass fast pyrolysis more or less started in October 1980, when the Solar Energy Research Institute (today NREL) organized a specialists’ workshop on fast pyrolysis of biomass in Copper Mountain, Colorado. Workshop chairman James Diebold believed he had brought together most of those who were working, or had published on fast pyrolysis of biomass (31 participants).

Research groups pioneering in the development of reactor technology during the eighties and nineties of the past century were those in SERI, Colorado, USA (Diebold and Scahill; ablative vortex reactor), the University of Western Ontario Canada (Bergougnou, Graham, Freel, Huffman, Mok; circulating fluidized bed), the University of Waterloo, Canada (Scott, Piskorz, Radlein, Czernik; bubbling fluidized bed), Laval University, Canada (Roy; vacuum moving bed), the University of Nancy, France (Villiermaux and Lédé; cyclone), Aston University, UK (Bridgwater and Peacocke; ablative plate), and the University of Twente, The Netherlands (Van Swaaij, Prins, Wagenaar, Venderbosch; rotating cone).

Fast pyrolysis [7] is characterized by a rapid biomass-particle heating, up to approximately 500 °C, followed by quickly cooling of the produced vapors to condense them to a maximum quantity of liquids. Usually, a dark-brown to black mobile liquid is formed with a heating value roughly equal to that of wood (that is about half the heating value of conventional fuel oil). All kinds of biomass materials can be transformed to fast pyrolysis liquid (bio-oil). The interest in the production of such a liquid is due to the opportunities for

- de-coupling of the fuel production (scale, time and location) from its utilization
- easy handling of a liquid fuel in further processing (transportation, pressurization, atomization)
- producing of a renewable fuel for boilers, engines, turbines and gasifiers.
- upgrading of the pyrolysis liquids to a refinery feed or fuel blending components
- integration in various biorefinery concepts, also for the conversion of lignin rich residues
- separation of the minerals from the process to be returned to the soil as a biomass nutrient.
- the production of biochar (soil improver) as a by-product.

Optimal conditions in terms of liquid yield include that: the pyrolysis reactor temperature should be around 500 °C, the biomass particle should be small (≤ 2 mm), the produced vapors should be separated from the char efficiently, and the produced vapors should be condensed at once in order to prevent secondary cracking to gaseous products. At such conditions the following products are obtained from e.g. pine wood: bio-oil: 75 wt. %, non-condensable gas: 10 to 15 wt. %, and char: 10 to 15 wt. %

Fast pyrolysis oil (bio-oil) is typically a dark red-brown to black, low-viscous liquid with a pungent (smoky) odor, and very specific physical properties. All the compounds in bio-oil are cracked products of the original biomass, and derived from (hemo)cellulosic and lignin structures. As the oil consists of fragments of the highly oxygenated carbohydrate and lignin polymers in biomass, it thus contains up to 35 to 45 wt.% oxygen on a dry basis. The main constituent is water. It is present in the bio-oil up to 35 wt.%, depending on the type of process and feed material, and the applied operating conditions. About two third of the water was bound in the biomass molecular structure, the rest being moisture contained in the feedstock. The high oxygen content of bio-oil can be noticed also from its heating value of around 17 MJ/kg (the oil is partially combusted already) which is just half of the value for fossil diesel. The bio-oil is acidic (pH~3), relatively polar in nature, and unstable. It has a density of around 1200 kg/m³.

The favorable physical appearance of an easily pumpable liquid is surprising, considering the fact that it is a pretty sensitive emulsion of either a-polar lignitic components in water, or vice versa. Because

bio-oil is a complex mixture of numerous compounds, varying in molecular weight from 50 up to 5,000 g/mole, it is very difficult to analyze and determine the key components. Around 300 different compounds have been identified, half of them regularly, by GC/MS and HPLC analysis. Even compounds with a boiling point above the process temperature are present in the oil; they are part of the pyrolysis vapor stream and apparently transferred from the reactor to the condenser as micro droplets (aerosols). The complexity of the pyrolysis oil hinders its use, the more so because any further (temperature) treatment causes the oil to re-polymerize. For specific applications, like in diesel or gasoline engines, upgrading of the oil is required.

In R&D, currently two approaches are followed for upgrading of fast pyrolysis liquids [8] to a product suitable for (co) feeding to a crude oil refinery, which is the way to reach the market for transportation fuel and chemicals. One is the catalytic hydro-deoxygenation of condensed pyrolysis liquids in a second processing step. Here the presence of a proper catalyst and hydrogen at high pressures (up to 200 bar) is essential to avoid the formation of char. Catalytic hydro-deoxygenation typically is carried out in two steps, one at 275 °C causing also separation of the water, and a second treatment at around 450 °C to achieve a higher degree of de-oxygenation. Amongst the catalysts applied are Ru/C, Cu/Ni and the commercial ones CoMo and NiMo. Full deoxygenation can be achieved but at the expense of a very high hydrogen consumption.

The other way to produce a de-oxygenated oil is by applying catalysts directly in the fast pyrolysis process. This is called catalytic fast pyrolysis. Here catalyst particles can be mixed with the heat carrier material (usually sand) that is used in the fast pyrolysis process and re-circulated continuously from the pyrolysis reactor to the char combustor. It enables immediate contact of the primary vapors with the catalyst and also allows to vary the ratio of catalyst over heat carrier particles to adjust the degree of catalysis in relation to the final composition of the bio-oil. Moreover, the catalyst which is expected to lose its activity quickly in the pyrolysis reactor due to coke deposition, will be regenerated immediately when passing through the char combustor. Alternatively, the catalyst can be in a reactor positioned downstream the pyrolysis reactor for catalytic treatment of the vapor stream to the condenser. The catalytic reactor can then be operated independently and at various conditions. Besides, in this operation mode the catalyst will not be exposed to any biomass derived catalyst-poisoning components as they are left in the pyrolysis char and finally end up in the combustor cyclones. Materials used for catalytic pyrolysis so far are: conventional FCC catalyst, various H-forms of zeolites (Beta, Y, ZSM-5 and Mordenite), alumina, silica-alumina and, more recently, a range of modified MCM-41 mesoporous materials. The potential of catalytic fast pyrolysis is still under discussion. Results reported in the literature show a high production of water, gases and coke-on catalyst and just a low yield of the desired liquid product.

Biomass conversion in hot compressed water

In contrast to dry / dried feedstock, virgin biomass often contains a lot of water typically between 40 and 90 wt.%. Instead of drying the wet materials to below ca. 15 wt.% (required for stable storing) and subsequent use in processes as described above, these types of biomass may be converted in hydrothermal processes. Here, hydrothermal refers to conversion in water at elevated temperatures and pressures. The water does not only act as a solvent, but also as a reactant and/or a catalyst. Biomass is very reactive in water. The polar bonds of the polymeric biomass components are attacked by the polar water molecules, which are extraordinarily active at elevated temperatures and pressures. Hemicellulose and cellulose are thus hydrolysed quickly. Moreover, the degradation products of biomass are highly soluble in hot compressed water, which suppresses polymerization reactions and thus tar and coke formation. The direct beneficial consequence of water acting as a reactant and a solvent is that hydrothermal liquefaction or gasification produces no solids, such as char or coke. The pressure and temperature range relevant to the various hydrothermal processes can be shown in a

diagram of the vapour pressure curve of water; it ends up in its critical point of $T_c=374\text{ }^{\circ}\text{C}$, $p_c=22.1\text{ MPa}$. Some of the processes are further explained hereafter.

Hydrothermal carbonization (HTC) of biomass [9] essentially proceeds via dehydration and decarboxylation yielding a product with a calorific value of about 30 MJ/kg on a water and ash free biomass basis. Its elemental composition is similar to that of lignite. The carbon content and the properties of the resulting cokes strongly depend on the feed materials and the applied process conditions which typically include temperatures in the range of 170 to 250 $^{\circ}\text{C}$, residence times of 4 to 14 hours and (equilibrium) pressure of about 1-2 MPa. The yields of the desired carbonaceous product (often called hydrochar) can reach values of up to 70 wt.% and even higher if catalysts such as citric acid are used. The product has a calorific value increased by 15-20 % relative to the dry feedstock weight. About 80 to 85 % of the carbon remains in the hydrochar, about 10-15 % is transferred to the aqueous phase in the form of organic acids and other oxygen-rich products, and the remainder ends up in the gas phase. The solid product is formed mainly by two pathways: either by solid-solid reactions or by polymerization of intermediate degradation products of biomass decomposition.

Hydrothermal liquefaction (HTL) can be performed at temperatures of 300 to 350 $^{\circ}\text{C}$ and the corresponding pressures of 12-18 MPa. Reaction times are in the range of 5 to 20 minutes. It is important to note here that the yield of the desired liquid (biocrude) depends significantly on the heating rate that has been applied; high heating rates are definitely beneficial in that respect.

If compared to fast pyrolysis oil, HTL oils have a substantially reduced oxygen content (10 to 15 wt.%) and a higher calorific value (30 to 35 MJ/kg), but they are very viscous and usually do not become fully fluid until above 80 $^{\circ}\text{C}$. On a dry and ash free biomass basis, typically 45 wt.% of biocrude, 25 wt.% of gas (mainly consisting of CO_2), and 20 wt.% of water (formed in the reaction!) are obtained. In the separate aqueous phase, quite some organic compounds are dissolved. Like in the case of hydrothermal carbonization, the oxygen contained in the biomass is removed from the biomass as CO_2 and H_2O . The reason for the high CO_2 content is the water gas shift reaction, in which carbon monoxide formed as an intermediate reacts with excess water to form hydrogen and carbon dioxide. The hydrogen saturates the reactive intermediates, thus suppressing almost completely the formation of coke. The thermal efficiency of the HTL process is in the order of 80 %.

Hydrothermal gasification refers to generating a product gas either rich in methane or hydrogen. At supercritical conditions including temperatures around 600 $^{\circ}\text{C}$, hydrogen is the main product if homogeneous or heterogeneous catalysts are present to prevent char formation and facilitate the water gas shift reaction. In the region just above the critical temperature, from 374 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, methane formation is preferred. Here, typical hydrogenation catalysts are used. In the subcritical region, catalysts are required that increase the gas yield. The mineral components of the biomass remain in the aqueous effluent, avoiding expensive gas cleaning steps. However, the utilization or disposal of effluent water containing residual organic compounds is a challenge to further development of all hydrothermal conversion processes. Numerous studies on the use of new catalysts are being conducted to enable more control over the selectivity and yields of any desirable products, and decrease the amount of residual organic compounds in water.

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